



Batteries for Advanced Transportation Technologies (BATT) Program

Project Summaries

June 6-8, 2006

Non-Carbonaceous Anode Materials

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Unlike the several structure types and compositions of cathodes that are found in commercial lithium-ion batteries, such as layered LiMO_2 ($\text{M}=\text{Co}, \text{Ni}, \text{Mn}$), spinel $\text{Li}_{1+x}\text{M}_{2-x}\text{O}_4$ ($\text{M}=\text{Mn}, \text{Ti}$) and olivine LiFePO_4 , the anodes of these batteries are restricted almost exclusively to elemental carbon (graphite and hard carbons). Only recently has Sony Corporation introduced the first commercial lithium-ion battery product 'Nexelion' that contains an intermetallic Co-Sn (+ carbon) anode. The major limitation of metal/intermetallic electrodes, viz., the large volume expansion/contraction that occurs during cell charge and discharge is well known and much work has been conducted worldwide in attempts to overcome this problem. Despite this obstacle, progress is being made and work continues on metal/intermetallic systems, largely because they still hold promise for doubling (at least) the gravimetric and volumetric capacities of graphite for which the theoretical values are 372 mAh/g and 818 mAh/ml, respectively.

Our anode task therefore differs significantly from our task on cathodes; the latter being directed specifically to a new class of compounds that is showing particular promise for implementation in the next generation of commercial lithium-ion cells. Our approach to anode research is more broad based and exploratory as we attempt to learn and understand more about the characteristic features of a few selected intermetallic systems that we hope will lead us ultimately to a commercially viable system. During FY2006, we have focused our efforts on four central themes:

1. New materials in the ternary system Co-Sn-Cu
2. Surface studies of AlSb (in collaboration with K. Edstrom, Uppsala University, Sweden) and surface coatings of Cu_6Sn_5 .
3. Low temperature behavior of Cu_6Sn_5 and Cu_2Sb anodes in full cells with ATD Gen 2 cathodes and electrolyte.
4. Prelithiation of intermetallic and metal oxide insertion electrodes with FMC Corporation's stabilized lithium metal powder (SLMP) 'Lectro Max'.

Although copper is largely inactive toward lithium, we are drawn towards intermetallic systems containing this metal because copper foil is the anode current collector of choice in lithium-ion cells. We have identified the 'Heusler' phase Cu_2CoSn , which is isostructural with Li_2CuSn and Li_2CuSb that we have observed in our studies of Cu_6Sn_5 and Cu_2Sb electrodes, in which the [CuSn] and [CuSb] zincblende framework provides a three-dimensional host framework for lithium. The existence of Cu_2CoSn raises the possibility of generating quaternary " $\text{Li}_x\text{Cu}_{2-x}\text{CoSn}$ " compounds in a lithium cell. The Li-Cu-Co-Sn system, in which two components are inactive towards lithium (Co and Cu) and one is active (Sn), therefore may hold clues for enhancing the stability of complex, intermetallic mosaic structures to repeated lithium insertion/extraction.

In FY2007, we plan to continue our studies of the bulk and surface properties of Cu-based intermetallic materials. We plan to use solid state NMR to investigate the complex charge transfer reactions that occur during electrochemical cycling. Collaborators who assist in this task are: K. Edstrom (Uppsala University, Sweden); Y. Gao and M. Yakovleva (FMC Corporation); C. Grey (SUNY, Stony Brook – NMR studies).

Novel Anode Materials

M. Stanley Whittingham
SUNY at Binghamton

The goals of this project are to replace the presently used carbon anodes with safer materials that will be compatible with low cost manganese oxide and phosphate cathodes and the associated electrolyte. Specifically we plan to gain a better understanding of what limits the use of simple alloys as the anode. The initial focus was placed on crystalline tin materials, with the initial experiments being on pure tin foils. We are now exploring amorphous tin compounds, where the capacity appears to be much better maintained. We are also exploring low cost oxides that are not poisoned by impurities from the cathode, and the impact of the electrolyte salt and solvent on anode life and capacity.

Metal-Based Anodes. The present graphitic carbon anode used in lithium cells shows exceptional recycleability, but can pose safety problems under high charge rates. We initially investigated some simple metals, which form alloys with lithium, to determine whether they can substitute for carbon and to gain a better understanding of their capacity loss on cycling. These emphasized tin foil, which can be used in the pure state without the complications of side reactions from other anode components. Although this tin foil, which has a grain size of just a few 100nm, cycles without loss of capacity for over 10 cycles even at rates of 3 mA/cm², it then loses capacity rapidly in most cases. Reducing the dimensions to the micron level, by using expanded foils, did not remedy the loss (with K. Zaghib of HQ). We are working with R. Kostecki at LBNL to follow the surface behavior of the tin foil during cycling. We also explored the impact of incorporating an inert component, such as manganese as in Sn₂Mn. We are now exploring amorphous nano-size tin that shows no long-range crystalline structure. A second component apparently prevents the crystallization of the tin; in the case of the SONY anode this is the expensive cobalt and a little titanium. We have characterized this new anode material and found that this amorphous nanosize material cycles much better than crystalline tin. No catastrophic fall-off in capacity was observed after ten cycles, but the material contains roughly equal amounts of tin and the expensive cobalt. The challenge will be to replace the cobalt with a less expensive material(s) such as manganese that fulfills the same function of preventing crystallization.

Oxide-Based Anodes. We investigated the anodic behavior of some mixed manganese-vanadium oxides in the past, and are expanding that study to nano-sized manganese oxides based on the promising results presented on nano-sized silicon pillars and by the Amiens group of Tarascon on CoO. Specifically we are exploring nanosized fibers of MnO_x, and will compare them to the titanium oxide spinel anode. These fibers are showing a constant capacity of around 400 mAh/g, with no catastrophic failure after ten cycles as found for crystalline tin compounds.

We are thus refocusing our efforts on nanosize materials with low crystallinity, where apparently the small particle size can withstand the expansion and contraction on reaction without major decrepitation.

Collaborations are underway with Dr. Robert Kostecki (LBNL) and Dr. Pete Chupas (Argonne National Laboratory) to better characterize the materials. These will be particularly critical for these non-crystalline compounds.

Publication:

Quan Fan, Peter Zavalij, and M. Stanley Whittingham, "Anode Hosts for Lithium Batteries: Revisiting Tin and Aluminum," *Mater. Res. Soc. Proc.*, 2005, 835: K6.16.

New Battery Electrolytes Based on Lithium Fluorosulfonate and Fluorosulfonimide Salts

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BATT work at Clemson over the June 2005 – May 2006 period continued to focus on synthesis and characterization of lithium fluorosulfonate and fluorosulfonimide ionic melt electrolytes targeted for use in hybrid electric vehicles' batteries. A specific ionic melt electrolyte was determined to be optimal in terms of conductivity. This electrolyte was synthesized in amounts sufficient for follow-on testing and characterized in detail. DC polarization tests showed definitively that this melt electrolyte does not undergo salt concentration polarization as DC current is passed through it. This attribute should provide performance advantageous for a high-power battery. Cell testing equipment has been acquired and cell testing will commence shortly that will seek to provide experimental evidence for performance advantages offered by the ionic melt electrolytes.

Specific accomplishments over the reporting period are as follows:

- Completed synthesis, purification, and structural conductivity characterization of ionic melt electrolytes having the following structures:
CH₃O-(CH₂CH₂O)_n-CF₂CFHO-CF₂CF₂-salt where n = 7, 12, 17 and salt = SO₃Li, SO₂N(Li)SO₂CF₃, and SO₂N(Li)SO₂C₄F₉ (n = 12 only).
CH₃O-(CH₂CH₂O)_n-CF₂CFHO-CF(CF₃)CF₂O-CF₂CF₂-salt where n = 7, 12, 17 and salt = SO₃Li and SO₂N(Li)SO₂CF₃
Salt-CF₂CF₂O-CFHCF₂O-(CH₂CH₂O)_n-CF₂CFHO-CF₂CF₂-salt where n = 13, 22, 44 and salt = SO₃Li and SO₂N(Li)SO₂CF₃
CH₃O-(CH₂CH₂O)_n-CF₂CFHO-CF₂CF₂-SO₂N(Li)SO₂-CF₂CF₂O-CFHCF₂O-(CH₂CH₂O)_nCH₃ where n = 7, 12
CH₃O-(CH₂CH₂O)_n-C₆H₄-salt where n = 7, 12, 17 and salt = SO₂N(Li)SO₂CF₃.
- Determined that the ionic melt of structure **CH₃O-(CH₂CH₂O)₁₂-CF₂CFHO-CF₂CF₂-SO₂N(Li)SO₂CF₃** which we designate **IM550** has the highest ionic conductivity of all melts prepared.
- Completed HPLC and MS characterization of **IM550** to definitively show that the synthetic product is highly pure and is devoid of any unreacted polyether.
- Developed a simple solvent-free synthesis for **IM550** that can be repeatedly performed in 5-10 gram batches, and prepared **IM550** in several gram amounts for follow-up studies.
- Completed DC polarization studies (potentiostatic and galvanostatic) on **IM550** in Li₄Ti₅O₁₂ | electrolyte | Li₄Ti₅O₁₂ cells which prove that salt concentration polarization does not occur when passing DC current through the ionic melt electrolyte.
- Discovered unexpectedly low impedance for the Li₄Ti₅O₁₂ | **IM550** interface compared with the Li₄Ti₅O₁₂ | LiTFSI-in-polyether interface.

A primary milestone for the reporting period was to develop in-house testing capabilities for small cells. Testing hardware has been acquired and testing protocols are in the process of being implemented. Some cycle testing has begun as part of validation procedures for the testing hardware, and more will be pursued in summer / fall as hardware and test protocol validation is completed.

Physical Characterization of Polymer Electrolytes

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We have established that by using a polystyrene-*b*-polyethyleneoxide (PS-*b*-PEO) diblock copolymer we can combine the mechanical stability of PS with the ionic conductivity of PEO. We have made conductivity measurements on a range of PS-*b*-PEO diblock copolymers in order to understand and optimize the ionic conductivity in these materials. The diblock copolymers were synthesized to access a large range of PEO molecular weight and volume fraction in the diblock system. We have characterized these systems by using GPC, NMR, and SAXS. We have also made AC impedance measurements on LiTFSI/copolymer mixtures. These measurements have shown very interesting results. The data indicate a lack of correlation between the ionic conductivity of these electrolytes and the volume fraction of PEO in the system, but a positive correlation between the ionic conductivity and the PEO molecular weight in the copolymer. This result, although somewhat counterintuitive, is very encouraging as it allows us to optimize the ionic conductivity of the electrolyte by simply changing the molecular weight of the PEO block in the copolymer.

We have also addressed the engineering issues with the processing of the electrolyte for the fabrication of a scalable membrane electrode assembly. Initially, the brittleness of our low molecular weight PS-*b*-PEO-based electrolyte had posed a challenge in its implementation. We have solved this problem by synthesizing higher molecular weight PS-*b*-PEO diblock copolymers that facilitate the hot pressing of flexible thin (50-100 μm) films. In addition, we have also synthesized a polystyrene-*b*-polyisoprene-*b*-polyethyleneoxide (PS-*b*-PI-*b*-PEO) triblock, thereby adding a rubbery polymer to the matrix and making it more flexible without any significant loss of ionic conductivity.

In order to characterize the PS-*b*-PEO based electrolytes we have performed a few experiments with non-blocking Li electrodes using both DC and AC voltages. With the help of these experiments we were able to identify a good design for the membrane electrode assembly (MEA), and its fabrication process. We have designed a hermetic chamber that can hold up to 20 such MEAs in an argon atmosphere for a parallel comparative analysis. We have established the process of depositing Li directly onto our electrolyte films, minimizing the interfacial resistance issues. We are in the process of testing Li-deposited electrolyte membranes in our new set-up using both DC and AC voltages. The preliminary results indicate a good cycling performance for the Li/PE/Li cells.

Anodes – An Investigation of the Stability of the Lithium Metal Interface

Alan West
Columbia University

This new project is an attempt to understand the mechanism of dendrite formation during charging of a secondary lithium battery. The mechanism for dendrite formation during the deposition of other metals (for example copper) is well understood, dendrites propagate rapidly as the deposition current approaches the limiting current. However, dendrites form at currents well below the limiting current during lithium deposition, and the exact mechanism is unclear.

We have coordinated with Gao Liu at LBNL to build the necessary laboratory set-up to conduct lithium deposition experiments. We have purchased and set up a tabletop glove box, a swagelok test cell, and high-purity electrolytes. Data from cyclic voltammetry and cell cycling experiments match well with published results. We believe we can gain insight on lithium dendrite formation by studying the deposition of lithium on a copper substrate. We plan to deposit lithium using potentiostatic and galvanostatic methods, as well as examining the deposit using EIS during various stages of cell cycling. The copper substrate can easily be removed from the glove box in a sealed Ar atmosphere in order to study the lithium deposit by an optical microscope, SEM, or a profilometer. We now consider Milestone 1 - to build the experimental test setup and determine the methods to characterize dendrite growth - to be completed.

Recently, we have started work on Milestone 2 - quantifying the influence of electrolyte properties and deposition conditions on dendrite formation and growth. Potentiostatic deposition experiments show an increased deposition rate with an increase in applied voltage. Results from chronoamperometric studies of lithium deposition in nonaqueous electrolytes containing varying PC to DMC ratio are presented. Since PC is a cyclic molecule and DMC is a linear molecule these results help to explain the effect of the solvent molecules on lithium deposition.

Also, we have started to micro-fabricate a cell to clearly observe *in situ* the lithium/electrolyte interface. It is our hope that observing the formation and propagation of lithium dendrites will lead to new observations about the mechanism of their formation.

Diagnostics - Interfacial and Reactivity Studies

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A homologous series of alkyl mono- and dicarbonate lithium salts was synthesized with the purpose of simulating the surface reduction products of the electrolyte solvents commonly used in Li-ion batteries. The physicochemical properties of these model compounds were then characterized to establish a reliable database for comparison with characteristics of reduction products forming the SEI layer in electrodes in Li-ion batteries. The physicochemical properties measured and reported on here include Fourier transform infrared (FTIR) spectra, proton NMR, X-ray photoelectron spectra, X-ray diffraction patterns, and thermal decomposition (TGA) and Li-ion conductivity data. Some comparisons to experimental data from the SEI layers in battery electrodes are also presented.

Molecular Simulations of Electrolytes and Solid-Electrolyte Interphase Components

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University of Utah

The goal of this project is to accurately predict ion transport, structure and mechanical properties of electrolytes and solid-electrolyte interphase (SEI) components utilizing molecular dynamics (MD) simulations. We have focused on understanding the underlying physical mechanisms leading to poor lithium transport in secondary lithium cells with an emphasis on improving performance. Specifically, we are carrying out MD simulations aimed at understanding:

- high SEI layer impedance of Li-ion cells with liquid electrolytes at low temperature
- poor lithium transport in ionic liquids and single ion conductor (dry and gel) polymer electrolytes
- barriers associated with lithium transport from electrolytes to the SEI layer and graphite

MD Simulations of Components of the SEI layer

Alkyl carbonates are believed to be major components of outer part of the SEI layer. Importantly, interfacial resistance, often associated with transport in/to the SEI layer, has been found to dominate lithium transport for liquid carbonate-based cells (Gen2 and Gen3 chemistry within the ATD program) at low temperature. We have performed MD simulations of lithium methyl carbonate ($\text{LiMC} = \text{LiCH}_3\text{OCO}_2$) and dilithium ethylene dicarbonate ($\text{Li}_2\text{EDC} = \text{LiCO}_2\text{OC}_2\text{H}_4\text{OCO}_2\text{Li}$) in order to understand their structure and lithium transport. The predicted conductivities of Li_2EDC and LiMC at elevated temperature (≈ 450 K) were found to be comparable to conductivities of liquid electrolytes such as EC/LiTFSI. At lower temperatures, however, conductivities of Li_2EDC and LiMC were significantly lower than for liquid electrolytes. The extrapolated (from higher temperature simulations) difference in conductivity between Li_2EDC and EC/LiTFSI was found to be four to five orders of magnitude at room temperature and more than seven orders of magnitude at -30°C , identifying glassy regions of Li_2EDC and similar alkyl carbonate compounds in the SEI layer as possible sources of high interfacial resistance at low temperature.

Transport in Ionic Liquids and Single-Ion Conductor Polymeric Electrolytes

We have utilized MD simulations to predict lithium transport and study lithium transport mechanisms in a number of ionic liquids and single-ion conductor polymeric electrolytes including (1) TFSI-anions tethered to ethylene oxide oligomers ($\text{EO}_n\text{TFSI}^-\text{Li}^+$) in close collaboration with the Clemson group, (2) polymeric electrolytes with oligoether/carbonate solvating groups and TFSI⁻ anions attached to a comb-polymer side chains in collaboration with J. Kerr group and (3) room temperature ionic liquids such as pyrrolidinium⁺TFSI⁻ and imidazolium⁺TFSI⁻ doped with LiTFSI. Electrolytes (1) and (2) exhibit the highest lithium conductivities observed to date for materials that do not develop concentration polarization during battery operation, while the LiTFSI-doped room temperature ionic liquids (3) combine negligible vapor pressure, high thermal and electrochemical stability with high overall conductivity. Our MD simulation predictions yield conductivities and ion self-diffusion coefficients and their temperature dependence in excellent agreement with available experimental data for these materials. Our simulations have led to important insight into Li^+ conduction mechanisms in these materials, opening new possibilities of ionic liquid and single ion conductor design. Particularly promising are materials where emphasis is placed on Li^+ transport through exchange of TFSI-anions instead of transport through exchange of strongly complexing non-ionic solvents such as ethylene oxide oligomers.

Property Measurements in and Optimization of Lithium-Ion Batteries

John Newman

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Lithium-ion batteries must be optimized for cost, calendar life, safety, power requirements, and a wide range of operating temperatures. Mathematical modeling and property measurements assist us in understanding these systems and the processes that limit battery performance. These models help to improve cell performance through optimization of cell geometry and examination of the impact of different parameters on cell performance. Accurate property measurements are necessary in order to develop accurate models and to compare the performance of different chemistries. Our work involves the characterization of electrolyte transport through the development of new and more accurate methods for measuring thermodynamic and transport properties in Li-battery electrolytes. We have adapted the method of restricted diffusion to measure diffusion coefficients in lithium-battery electrolytes using UV-Vis absorption. The use of UV-Vis absorption provides a simple alternative to more arduous experiments that may be prone to side reactions. In addition, through the use of a system model in collaboration with Venkat Srinivasan, we have provided parameters for an optimized lithium iron phosphate/lithium titanate spinel cell. This pair of electrode chemistries is promising due to the moderate potentials of the anode and cathode. Side reactions may be avoided, providing enhanced calendar life and safety. Lithium iron phosphate is also inexpensive. We have also begun work optimizing the design of an asymmetric-hybrid system with the Energy Storage Group at Rutgers University. This technology attempts to bridge the gap in energy density between a battery and supercapacitor. In this system, the positive electrode (activated carbon) stores charge through a reversible, nonfaradaic adsorption of anions on the surface. The negative electrode is nanostructured $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which reversibly intercalates lithium.

To obtain accurate results with our models, we depend on accurate measurements for the necessary transport properties in the electrolyte. Diffusion coefficients, combined with the conductivity and transference numbers of the electrolyte are key determinants of battery performance. A low value of the diffusion coefficient of the electrolytic salt can limit charge and discharge rates and lead to concentration gradients in the electrolyte during cell operation. These concentration gradients can promote side reactions and ultimately lead to cell failure. A new adaptation of the restricted-diffusion method has been developed for measuring diffusion coefficients in Li-ion battery electrolytes.

The technique of restricted diffusion involves the establishment and subsequent relaxation of a concentration gradient in a vertical cell. At adequately long times, the concentration profile relaxes exponentially with time. This relaxation is monitored in order to obtain the diffusion coefficient for the system. Here, UV-Vis absorption is used to monitor the relaxation of a concentration gradient that has been physically introduced. The technique evaluates the change in concentration at one point one sixth of the liquid column height in distance from the bottom of the column. The experimental setup was designed to eliminate the effects of vibration. We began by measuring the diffusion coefficient in LiPF_6 solutions in acetonitrile. Results indicate that the diffusion coefficient of LiPF_6 in acetonitrile is approximately one magnitude higher than that in carbonate solvents.

R&D for Advanced Lithium Batteries

John Kerr

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A priority has been the chemical reactivity and the effect of impurities on the reactivity of electrolytes and cell behavior. In particular, the measurement of water content of not only electrolytes but also of the solid components of the cells has been targeted as it is clear from results of other BATT workers that moisture entrapped in electrode components contributes to impedance rise. As part of this work, we are attempting to determine how the water interacts with the electrolyte components, what reactions may be initiated by water and other protic impurities. It is the objective of these efforts to quantify an acceptable level of moisture in the cell components that will allow cells to be built reproducibly with predictable performance. In this we hope to assist the cell development task in providing specifications for control of the cell building environment. In order to work with very dry systems it is necessary to place the Karl-Fischer titrator in a glove box.

We have confirmed results obtained in industrial laboratories that show that the residual moisture in the electrolyte solvents (ethylene carbonate/ethylmethyl carbonate) decreases upon addition of the LiPF_6 and that the acidity increases over time. Control measurements performed with LiTFSI salt show neither a decrease in moisture content nor any increase in acidity over time. Presumably the acid produced with LiPF_6 is HF which results from the reaction of water with PF_5 . It is unclear as yet as to how the HF reacts with the electrolyte components. The introduction of PF_5 into dry solvent components ($<10\text{ppm H}_2\text{O}$) shows a considerable degree of transesterification and ring-opening of ethylene carbonate and production of phosphoryl fluoride at ambient temperatures, depending upon the concentration of PF_5 . Work is continuing on quantifying the reaction rates and how the presence of impurities may affect the reactivity, including impurities such as excess LiF that may inhibit the reactions. Higher molecular weight products have been detected amongst the products from electrolyte decomposition. These are consistent with the production of organofluorophosphates which ultimately degrade all the way to phosphate and fluoride ion. These reactions may be implicated in the growth of the interfacial impedance at the electrodes that limit cell life.

DSC measurements have been carried out on liquid and gel polymer electrolytes in the presence and absence of electrode components to ascertain abuse tolerance. Some improvements in stability with PEO-type gels are observed but not in the presence of metal oxide cathode materials. For these experiments we are comparing LiPF_6 electrolytes with LiTFSI controls which appear to be more stable. In all cases, however, volatile, flammable vapors are produced which are of concern for abuse tolerance. In order to avoid the flammable solvent issue we are investigating the use of ionic liquids in conjunction with redox polymer electrode coatings on carbon electrodes. These systems have no vapor pressure, are essentially non-flammable and may represent a viable solution to the abuse tolerance problem for HEV applications. The initial thermal behavior is encouraging enough to consider further development of the concept for HEV where the discharge capacity requirement is small.

Cathodes, Anodes, Cell Development

Thomas J. Richardson

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This task addresses issues important to development of safe, cost-effective lithium ion batteries with adequate energy and power densities and extended lifetimes. These include chemistry and electrochemistry of electrode materials as well as general issues of component structure and stability.

Cathodes: A detailed investigation of the mechanism of the LiFePO_4 -to- FePO_4 phase transformation has been undertaken. While there has been considerable speculation concerning the nature of electronic and ionic conduction in these phases, and it is generally accepted that the latter is confined at room temperature to tunnels oriented parallel to the b -axis (space group $Pnma$), most models for the interconversion of these phases assume a spherical “shrinking core” of one phase surrounding the other. The strong anisotropy of the structure and the implication that only the ac surfaces are electrochemically active has also been ignored in evaluation of conductivity and diffusion coefficient measurements.

The well-characterized, highly crystalline LiFePO_4 samples required for this work were prepared by hydrothermal methods. The effects of process temperature and time, initial pH of the reaction mixtures, and reactant concentrations were examined. Batches of crystals with narrow size distributions and varying morphologies were reproducibly obtained under different conditions. Partial chemical delithiation of these crystals by treatment with solutions of elemental bromine produced largely intact crystals containing both phases.

Ex situ SEM and TEM images along with selected area electron diffraction patterns obtained from partially oxidized crystals showed an unusual and well-defined arrangement of alternating domains of LiFePO_4 and FePO_4 aligned perpendicular to the a -axis. A mechanism was proposed involving a narrow disordered (but not amorphous) non-stoichiometric transition zone in the bc plane, which proceeds in the direction of the a -axis, consuming one phase and producing the other in its wake, with Li ions and electrons moving in or out of the transition zone in the b direction.

Anodes: Lithium alloys such as Li-Sn and Li-Si are attractive candidates to replace graphite due to their very large theoretical capacities. In practice, however, these materials suffer from significant irreversible capacities and poor cycle life. These problems arise from the substantial atomic rearrangements and large volume changes accompanying first-order phase transitions which expose fresh surfaces to electrolyte, and isolation of active material by fracturing. Solid solution lithium alloys with continuous stress-free volume changes and the presence of a driving force for internal homogeneity could avoid these difficulties and reduce the tendency for dendrite formation.

We have begun an investigation of Li-Mg alloy anodes, which offer a very wide single-phase compositional range. A novel method of preparation of Li-Mg cermet containing inert Mg_3N_2 inclusions has been developed and shown to produce electrodes with performance superior to that of the pure alloys.

Diagnostics - Electrode Surface Layers

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Our first objective was to develop and evaluate microwave plasma-assisted (MPA) synthesis of graphitic carbon films on LiFePO_4 to improve high-rate performance and cycle/calendar life of composite cathodes. The presence of a sp^2 -coordinated carbon coating, which exhibits the best electronic conductivity determines electrochemical properties of LiFePO_4 (collaboration with M. Doeff). Preliminary experiments revealed that interaction of some organic precursors with low-pressure Ar-plasma and electromagnetic radiation led to formation of highly crystalline graphitic carbon films with an excellent electronic conductivity.

We initiated and optimized the microwave plasma-assisted carbon-coating process to obtain electronically conductive and uniform thin films of graphitic carbon directly on cathode active material powders. LiFePO_4 (collaboration with K. Zaghib), $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powders were microwave-coated with a thin film of conductive carbon. The film comprises of densely packed ~ 50 nm particles, which consist of $\sim 40\text{\AA}$ graphene domains. Interestingly, the graphitic structure of the carbon film is very similar to the carbons pyrolyzed at temperatures above 1200°C . However, XRD and Raman spectra of the microwave carbon-coated cathode materials show no indication of structural damage due to overheating.

A preliminary electrochemical evaluation of the LiFePO_4 and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ carbon-coated powders was carried out to determine the impact of carbon coating on electrode impedance (collaboration with M. Doeff). Electrochemical charge/discharge tests of the composite LiFePO_4 cathodes vs. Li anode showed a significant improvement of material utilization and power performance of the MPA carbon-coated powder compared to uncoated electrodes. Electrochemical characterization of composite $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathodes also showed improvement of the electrode power performance and cycle life. The comparative experiments of MPA-coated electrodes are still being continued and a full evaluation of this technology is expected to be completed by the end of June 2006. An U.S. Patent application referring to this invention was filed by LBNL in May 2006.

Our second objective was to complete in-depth diagnostic studies of the mechanism of carbon retreat. To accomplish that goal, composite $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathodes enriched with ^{13}C soft carbon, which emulates physico-chemical properties of acetylene black, were manufactured, characterized, and tested at room temperature and 45°C vs. Li-metal anode in Swagelok model electrochemical cells. ^{13}C -sensitive Raman Microscopy analysis of the cell components was used to monitor qualitatively and quantitatively carbon distribution within tested cells and establish possible links with other detrimental phenomena.

Post-mortem micro-Raman analysis of the tested cathodes showed a noticeably higher surface concentration of the active material and lower surface concentration of the carbon additives. These results are in concert with our earlier diagnostic observations from commercial Li-ion batteries and model BATT cells. We found that only small amounts of fine carbon particles were carried away from the cathode. A modest amount of fine carbon particles trapped in the Celgard 2300 separator and traces of carbon additives in the electrolyte and at the surface of the Li anode were identified and characterized. The Raman spectra of the carried-away carbons clearly showed contributions from amorphous ^{12}C and ^{13}C . These amorphous carbons could be natural contaminants of the graphite and ^{13}C carbon black additives; they could result from mechanical processing during electrode manufacturing; or they could originate from gradual carbon particle delamination due to PF_6^- anion intercalation-deintercalation during electrochemical cycling. In summary, we postulate that the changes in the carbon additive distribution in composite cathodes are mainly responsible for the observed effect and account for the long-term capacity and high-rate performance loss of composite Li-ion cathodes.

Mathematical Modeling of Advanced Li-ion Chemistries

Venkat Srinivasan and John Newman
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The goal of this project is to use mathematical modeling, combined with experimentation, to provide insight into the operation of advanced Li-ion chemistries and help design them for a specific application. To date, we have modeled three cathodes namely, LiFePO_4 , $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (L333), and LiMn_2O_4 (spinel), and two anodes, namely, graphite and Li-metal. We have used these models to understand limiting mechanisms and to optimize performance to assess their ability to achieve the FreedomCAR performance goals for EVs and HEVs. This year, we have focused our modeling efforts on microscopic transport and developed a methodology to describe conduction in insulating/semiconducting materials. The methodology has been used to provide insight into the operation of LiFePO_4 cathodes. In addition, the optimization studies have been continued to understand the impact of using high-power graphite as an anode.

HEV optimization using high-power anodes: The previous optimization of the graphite-based systems showed that the performance was limited by the SEI resistance of the anode. Specifically, the anode used in the study (natural graphite) has area specific impedance (ASI) of $40 \text{ } \Omega\text{-cm}^2$. For comparison, the ATD Gen 2 anode has an ASI of $15 \text{ } \Omega\text{-cm}^2$. Therefore, the optimization was redone for this high-power anode. Results suggest that LiFePO_4 /Graphite cells can achieve power densities in excess of 3500 W/kg , when the particle size of the cathode is optimized.

Particle-level modeling of low-conductivity materials: The ability of LiFePO_4 to achieve extremely high-rates (see above) despite its low-conductivity ($\sim 10^{-9} \text{ S/cm}$) has been a source of interest in the scientific community. In order to provide perspective on this issue, a particle-level model was developed that describes diffusion and migration with Li^+ and e^- as charge carriers. The geometry chosen is that of a thin-pellet with a large area for lithium reaction with a smaller area for electron injection (similar to a spherical particle with small carbon content). The two phases in LiFePO_4 and their location are ignored in the model to keep the analysis simple. Model results show that the potential drop across the pellet is negligible (less than 100 mV) even for materials that have conductivity lower than that reported for LiFePO_4 . This small drop occurs because the current takes the path of least resistance and, therefore, transfers to the solution within a very short distance from the carbon. Consequently, transport of ions across the pellet occurs by a concentration gradient, not a potential gradient. The model shows that with proper cell design it is possible to make a high-rate battery from an insulating material.

Microscopic model of conduction in oxides: Reviewers of the June 2005 BATT review suggested that the models should begin to include the next level of details within the oxides. To this end, we have developed a methodology to describe transport of charge carriers (Li^+ and e^- and, possibly, other carriers) on lattice sites. The methodology is generic and should be applicable to many different materials. Equations were developed to correlate microscopic effects to performance. The methodology was applied to the LiFePO_4 system to understand the impact of lithiation/delithiation on the conductivity of the material. Specifically, modeling work on Gerd Ceder's group at MIT has indicated the formation of quasi-particles between the Li^+ and e^- resulting in a decrease in the charge carrier concentration. We have incorporated this effect into our model. The simulations when combined with experimentation should allow us to understand the conduction in this chemistry. Thin-film experiments are planned in the coming months to achieve this understanding.

Synthesis and Characterization of Cathode Materials for Rechargeable Li and Li Ion Batteries

Marca M. Doeff

Lawrence Berkeley National Laboratory

During FY 2005-2006, dramatic improvements in the performance of in-house synthesized LiFePO_4 with low carbon contents (~ 1.5 wt%) were achieved by the addition of pyromellitic acid (PA) and ferrocene during calcination. Low carbon content is critical to avoid unduly lowering tap densities. PA and ferrocene pyrolyze to form highly conductive coatings having low D/G (disordered/graphene) ratios as determined by Raman microscopy (with R. Kostecki and M. Marcinek, LBNL, diagnostics). Pressed pellet conductivities of LiFePO_4/C composites scale with rate performance in electrochemical cells and are inversely proportional to the D/G ratios. Energy filtered transmission electron microscopy (EFTEM) on a high-rate LiFePO_4 sample shows that a carbon coating about 5 nm thick is present on surfaces of primary particles, even in highly irregular agglomerates. The coatings adhere extremely well and do not spall off even after 100 or more electrochemical cycles (with H. Gabrisch, University of New Orleans, TEM). Pyrolysis of ferrocene/PA mixtures under LiFePO_4 synthesis conditions results in the production of highly strained graphite plates and/or multi-walled carbon nanotubes (MWCNTs), depending upon the Fe/C ratio. The presence of highly conductive MWCNTs should allow significant reduction of the amount of carbon that needs to be added to composite LiFePO_4 electrodes. Modeling shows that the number of nanotubes required to achieve percolation varies with geometric factors such as curliness, but can be less than 1 vol. % (with A. M. Sastry, University of Michigan, modeling). Mixing pre-made nanotubes into electrode slurries, however, is expensive, difficult, and raises health and safety concerns. Co-synthesis of nanotubes and LiFePO_4 bypasses these issues and appears to be feasible. (Milestone achieved, 6/06). Future work will be directed towards identifying nanotube structures (which determine conductivity), and optimization of nanotube/ LiFePO_4 systems (with A. M. Sastry).

The effect of storage at 55°C on manganese-containing electrode materials was also examined during FY2005-2006. Mn dissolution is a factor of surface area, average Mn oxidation state, structure, and details of substitution. Insertion of polar molecules from the electrolytic solution into the van der Waal's gaps of some layered materials and subsequent exfoliation, which leads to capacity fading upon cycling, also occurs; the extent of this depends upon the stacking arrangement ($\text{O}_2 > \text{O}_2/\text{O}_3$ intergrowth $> \text{O}_3$). The most robust materials appear to be Ti-substituted tunnel compounds, which show no tendency towards solvent intercalation, Mn dissolution, or capacity fading upon cycling at elevated temperatures (with Y. J. Park, Kyonggi University, South Korea, milestone achieved 1/06). The resistance to dissolution makes these high voltage materials good candidates for use with ionic liquid electrolytes (ILs) and metallic lithium anodes. Under some circumstances, pyrrolidinium-based ionic liquids can be used with lithium anodes without the occurrence of dendrite formation, but most common cathode materials dissolve in the ILs, limiting usefulness. Some future work will be directed towards determining the feasibility of developing lithium metal/IL/Ti-substituted tunnel compound systems (with A. Best, CSIRO, Australia).

Improving Cathode Capacity and Rate Capability

John B. Goodenough and Yun-Hui Huang

The University of Texas at Austin

Collaborator: Karim Zaghib

Institut de Recherches à Hydro-Québec, Canada

The universal motif of cathodes in lithium rechargeable batteries is the arrangement of immobilized redox centers of appropriate energy that are reversibly accessible by electrons from/to a current collector and Li^+ ions from/to the electrolyte. Immobilization ensures that the redox units do not transfer from the cathode to the electrolyte and subsequently poison the anode. Use of rechargeable batteries in HEVs or EVs requires, in addition to a large capacity, the ability to sustain high rates of charge and discharge over a considerable temperature range. Hydro-Québec and Phostech Lithium, Inc. coat their LiFePO_4 olivine particles with amorphous carbon. Their procedure removes $\gamma\text{-Fe}_2\text{O}_3$ impurities that impede Li^+ -ion transport by reducing all the iron to Fe^{2+} . The carbon-coated C- LiFePO_4 particles are conventionally mixed with electrochemically inactive carbon to provide electron transfer between particles and the current collector as well as PVDF as a binder of the composite mass. We have replaced these inactive additives with an electrochemically active, conducting polymer, polypyrrole (PPy), that not only provides electronic transport between the particles and the current collector, but also acts as a binder of the cathode mass that is penetrated by the electrolyte. This year we have tested the case of PPy with several oxide cathode materials that do not have a carbon coat and compared the results with those for C- LiFePO_4 . These tests have demonstrated that attachment of the polymer to the oxide particles via the carbon coat is essential for good electronic transport between the polymer and the oxide. We have also shown that the optimum ratio of PPy to C- LiFePO_4 is about 20 w% and that the capacity of this composite is larger than that of a conventional C- LiFePO_4 :C:PTFE 75:20:5 w%, the difference increasing markedly with increasing rate of charge or discharge. The cells with C- LiFePO_4 /PPy cathode composite cathodes sustained charge and discharge cycles at the 10C rate for over 50 cycles and remained stable even at the 20C rate.

Investigation of the layered $\text{LiNi}_{0.5+x}\text{Mn}_{0.5-x}\text{O}_2$ cathode materials showed better results with smaller values of x . We attained a better increase in capacity by coating with Al_2O_3 than with LiAlO_2 , and we plan to explore coating with $\text{Li}_{1-x}\text{AlO}_{2-x}\text{F}_x$. Our strategy here is to develop a coat permeable to electrons and Li^+ ions that prevents holes generated in the $\text{Ni}^{4+}/\text{Ni}^{3+}$ redox couple by Li^+ -ion removal from reaching the surface.

Novel Cathode Materials

M. Stanley Whittingham
SUNY at Binghamton

The primary goals of this project are to find (a) lower-cost and higher-capacity cathodes, exceeding 200 Ah/kg, and (b) high-rate HEV compatible cathodes, both of which are based on environmentally benign materials. The major efforts are being focused on stabilized layered manganese dioxides, and on building a base case cathode system using LiFePO_4 against which the manganese and other cathodes will be compared. These goals address the two systems: (a) Li-Ion high voltage, high energy and (b) low voltage high stability.

Lithium Iron Phosphate. Lithium iron phosphate is a low cost and higher stability cathode material with potential application in many systems, ranging from power tools to hybrid electric vehicles. In 2005 we completed our study on lithium iron phosphate as a base case system. LiFePO_4 is a very stable cathode material above 1.5 volts, and cycles exceptionally well; the capacity may be enhanced to 100% by either raising the temperature or lowering the power output. However, it would be advantageous if lower cost ways could be found to manufacture this inherently low-cost compound. We have revisited the low temperature hydrothermal approach. We have found that by using temperatures in excess of 175°C we can make material that is structurally pure, and with no lithium iron disorder. Moreover, when a reducing agent such as ascorbic acid and/or sugar is added we obtain pure ferrous material. The addition of these carbonaceous compounds also enhances the conductivity of the material, as does the incorporation of carbon nanotubes. Using such material we can obtain electrochemical capacities comparable to those of the high temperature synthesized compound, with close to 100% removal of lithium in the first charge. The capacity retention of these hydrothermal materials is excellent, with essentially no loss found. We plan to make smaller particle sizes. We continue our efforts on other phosphates but none yet have an overall advantage over the Olivine phase.

Stabilized Layered Manganese Dioxides. The layered nickel/manganese system, $\text{Li}_{1+x}[\text{Ni}_y\text{Mn}_y\text{Co}_{1-2y}]_{1-x}\text{O}_2$, has been studied for $0.33 \leq y \leq 0.5$ to determine the optimum composition, the nature of the electrochemically active specie, the role of cobalt, and to compare capabilities against LiFePO_4 .

- We found that some Ni in the Li layer is advantageous, preventing phase change during cycling, and thus enhancing cycle capacity retention.
- To understand the first cycle capacity loss, and to determine why maximum capacity is not obtained, we have been investigating the behavior of these interlayer Ni ions. We found that this Ni in the Li layer is impacted as soon as the cell charging begins; it either moves from its octahedral interlayer site or is oxidized to Ni^{3+} or Ni^{4+} before the Ni in the transition metal layer is oxidized. If it irreversibly moves, then this might be a possible cause of the first cycle capacity loss.
- We investigated the impact of initial Li content on the capacity and cyclability of the $\text{Li}_{1+x}[\text{Mn}_y\text{Ni}_y\text{Co}_{1-2y}]_{1-x}\text{O}_2$. For formation temperatures of between 800 and 900°C , the slightly Li-deficient cells show the best cyclability when the cells are cycled at a constant rate. When lower charging rates are used, the capacity is increased particularly for the Li rich compounds. We will test the best of these materials under the HEV regime and increase the Mn content.

Collaborations and discussions are ongoing with Dr. Won-Sub Yoon (BNL) on in-situ structural measurements of cells, with Profs. Clare Grey (SUNYSB) and Gerd Ceder (MIT) on the transition metal distribution in the oxides both as synthesized and on cycling, and with Prof. Yang Shao-Horn (MIT) on the microstructure and transport properties of these cathode materials.

Publications acknowledging DOE-BATT support:

1. J. Chen and M.S. Whittingham, "Hydrothermal Synthesis of Lithium Iron Phosphate," *Electrochem. Commun.*, 2006, 8: 855-858.

Advanced Spinel Manganese Oxide Cathodes

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Spinel manganese oxide cathodes offer the important advantages of low cost and high rate capability compared to other cathode systems, but they suffer from severe capacity fade at elevated temperatures. With an aim to develop a firm understanding of the factors influencing their capacity fade and utilize the understanding to develop high performance compositions, we have been focusing on the structure-composition-performance relationships of spinel manganese oxide compositions with both cationic and anionic substitutions in the spinel lattice. While the cationic substitutions invariably lead to a decrease in capacity despite an improvement in capacity retention, the substitution of fluorine for oxygen in the cation substituted spinel oxides helps to counter the decrease in capacity due to a reduction in the manganese valence. However, the challenge in incorporating significant amount of fluorine into the spinel lattice is the volatilization of fluorine at the conventional synthesis temperature of 800°C. To overcome this difficulty and maximize the fluorine content, we have developed a procedure in which the cation-substituted oxides already synthesized at higher temperatures (~ 800°C) is fired with ammonium hydrogen fluoride at a moderate temperature of 450°C for a short time of 5 h. With this procedure, we have synthesized and characterized several spinel compositions such as $\text{LiMn}_{1.8}\text{Li}_{0.2}\text{O}_{4-z}\text{F}_z$ and $\text{LiMn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_{4-z}\text{F}_z$. Based on the analysis of the oxidation state of the transition metal ions by a redox titration and an assumption of the total anion (O + F) content to be 4.0, we have been able to incorporate fluorine contents of $0 \leq z \leq 0.2$ into the lattice.

The fluorine substituted compositions exhibit up to 20 mAh/g higher capacities and better storage characteristics and cyclability at 60°C compared to the corresponding oxide counterparts while maintaining similar rate capabilities. The superior capacity retention, rate capability, storage characteristics, and power retention (as determined by PNGV L-HPPC tests) with a lower irreversible capacity loss of compositions such as $\text{LiMn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_{4-z}\text{F}_z$ compared to those of the conventional LiMn_2O_4 cathode are found to be due to a significantly lower amount of manganese dissolution and a much smaller lattice parameter difference Δa between the two cubic phases formed during the charge-discharge process; the capacity fade at 60°C decreases with decreasing Mn dissolution, which decreases with decreasing Δa . Also, *in situ* X-ray diffraction data collected in collaboration with the Brookhaven National Laboratory show a reduction in Δa on going from $\text{Li}_{1.04}\text{Mn}_{1.96}\text{O}_4$ to $\text{LiMn}_{1.8}\text{Li}_{0.2}\text{O}_{3.79}\text{F}_{0.21}$ and $\text{LiMn}_{1.85}\text{Li}_{0.075}\text{Ni}_{0.04}\text{Al}_{0.035}\text{O}_4$, confirming the relationship between capacity fade and Δa .

With an aim to develop a broader understanding of the impact of metal ion dissolution from cathodes, we have also compared the amount of transition metal ion (Mn, Co, Ni, and Fe) dissolution from spinel, layered, and olivine oxide cathodes. Layered and spinel oxides containing Mn^{4+} such as $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ and $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ show lower manganese dissolution than spinel LiMn_2O_4 and orthorhombic LiMnO_2 containing Mn^{3+} , confirming that manganese dissolution is related to the disproportionation of Mn^{3+} . Advantageously, despite the presence of a significant amount of Mn^{3+} , the cation-substituted oxide and oxyfluoride spinel compositions such as $\text{LiMn}_{2-x-y}\text{Li}_x\text{Ni}_y\text{O}_4$ and $\text{LiMn}_{2-x-y}\text{Li}_x\text{Ni}_y\text{O}_{4-z}\text{F}_z$ exhibit much reduced manganese dissolution, but slightly higher than that found with the Mn^{4+} spinel cathodes.

Furthermore, surface modified layered oxide cathodes such as $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$, which belong to a solid solution series between layered Li_2MnO_3 and $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$, have been found to show a remarkably high capacity of 285 mAh/g with a reduced irreversible capacity loss of 40 mAh/g compared to the unmodified counterparts. Surface modification with Al_2O_3 suppresses the reaction between the cathode surface and the electrolyte and thereby decreases the irreversible capacity loss and increases the reversible capacity.

Publications: 5 journal articles have been published or accepted for publication this grant year.

Novel Cathode Materials
Michael M. Thackeray
Argonne National Laboratory

During FY2006, we continued to exploit the concept of using integrated 'composite' structures containing a layered Li_2MnO_3 component in our endeavor to develop novel, low cost, high-energy and high-power electrodes. We have demonstrated this concept with materials that can be formulated as $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$ for 'layered-layered' systems, and $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiM}_2\text{O}_4$ for 'layered-spinel' systems ($\text{M}=\text{Mn}, \text{Ni}, \text{Co}$). The strategy is to use the Li_2MnO_3 component to enhance the structural stability of a conventional layered LiMO_2 electrode or a spinel LiM_2O_4 electrode and to activate part of the Li_2MnO_3 component ($\text{Li}_2\text{O} \bullet \text{MnO}_2$) by removing Li_2O at high potentials (4.5-4.8 V vs. Li^0) during the initial charge, thereby generating a high-capacity (240-250 mAh/g), manganese-based electrode. These materials are, therefore, of particular interest for 'plug-in' HEVs and pure EVs where high energy is a critically important factor. Most of our effort in FY2006 was focused on evaluating 'layered-layered' systems because they show the greatest promise of the two systems thus far.

'Layered-layered' $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$ systems are generally referred to in the literature as 'lithium-rich' layered compounds because the $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$ formula can be normalized and rewritten more simply in standard layered notation as $\text{Li}_{1+x}\text{M}_{1-x}\text{O}_2$ (in which M now includes both the Mn and M ions of $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$). The removal of two lithium ions (as Li_2O) from the Li_2MnO_3 component during charge and the reintroduction of only one possible lithium ion into the resulting MnO_2 component during discharge, results in an unavoidable irreversible capacity loss on the initial cycle, some of which can be used to offset the irreversible capacity loss encountered at the negative electrode. We have previously demonstrated that preconditioning the electrode with acid to remove Li_2O from the Li_2MnO_3 component offsets the first-cycle irreversible capacity loss. Our recent work on $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$ systems has highlighted: 1) the participation of the manganese ions from the individual Li_2MnO_3 and LiMO_2 components in the electrochemical reaction, and 2) the role that proton-exchange plays in the chemical activation process. The activation of $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$ electrodes, whether chemical or electrochemical, leads to an increase in cell impedance and capacity fade at high rates. We have made progress in countering the damage inflicted on these activated electrodes by modifying the parameters of acid treatment. To complement our experimental investigations, we have initiated theoretical modeling studies of cathode phenomena brought about by acid treatment, such as dissolution and H^+ -ion exchange.

The significant momentum gained in this task provides strong motivation to continue our evaluation and optimization of composite electrode structures in FY2007. We will focus on: 1) cation substitution; 2) surface stabilization; 3) full cell performance (vs. graphite and intermetallic anodes); 4) and low temperature behavior. We will maintain our collaborations with S. Hackney (Michigan Tech. Univ. - HRTEM); C. Grey (SUNY, Stony Brook - NMR); X. Yang (Brookhaven Nat. Lab. - in situ XRD); M. Anderson (University of Wisconsin - surface coatings); P. Bruce (St. Andrews Univ., UK - in situ neutron diffraction); W. David (Rutherford Appleton Laboratory, UK - pdf analyses).

First Principles Calculations and NMR Spectroscopy of Cathode Materials

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The objectives of this project are to determine the effect of structure on stability of cathodes and explore rate limitations and its relation to the structure.

We have achieved a key milestone in understanding the chemical and structural factors that affect the rate capability of layered intercalation compounds and have proceeded to use that knowledge to develop a $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$ material with superior rate performance.¹ $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$ is environmentally friendly, has the potential to be low cost, and has some of the best thermal stability in the classes of Ni-Mn-Co containing layered materials, but was previously thought not to be capable of sustaining high charge and discharge rates. Using first-principles computations we have evaluated the factors that affect this rate performance. The results show that an ideal material with a 50% content of Ni^{2+} should have intrinsically high Li mobility, as the activated state for Li migration near Ni^{2+} is lower in energy than near any other cation tested. The interslab space (i.e., the distance between the oxygen layers that surround the Li layer) is found to be the largest factor influencing the Li mobility. Even minor changes of $\pm 2\%$ in this slab distance were found to have major implications for the activation barrier of Li motion. As this layer-to-layer distance grows, the space in the activation site increases and the activation energy for Li motion decreases dramatically. This explains why $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$ prepared via traditional solid-state methods does not have good rate capability: The large amount of Li/Ni exchange between the layers (as seen in our NMR and diffraction studies), reduces the Li-slab distance (and more importantly, reduces its opening upon delithiation). To test this hypothesis a well layered material with significantly less Li/Ni ion-exchange was prepared by ion-exchanging it from a $\text{Na}(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$ precursor. NMR on the ion-exchanged material confirms that very little Li is present in the transition metal layer. Initial rate tests show that this material has excellent rate capability.

Experiments (diffraction, NMR, pair-distribution function analysis) and theory were used to compare the long-range and local structure of the traditional and ion-exchanged materials before, during, and after cycling. Both materials show non-random distributions of cations in the transition metal layers and a strong tendency for Ni-Mn interactions and Mn-Mn and Ni-Ni avoidance. The Li/Ni exchange in the traditional material has further implications for the structural changes that occur on cycling this material: The Li ions in the transition metal layers in the traditional material can be removed on charging to high voltage, the Ni-ions in the Li-layer migrating to fill the vacancies left by the Li, upon oxidation to Ni^{4+} . These Ni ions are not necessarily stable on discharge, with some of the Ni migrating back into the Li layers. We believe that we now have a much deeper understanding of the structural and chemical factors that control rate in layered oxides. We are now planning to use these concepts to make materials with considerably better rate performance.

We continue to collaborate with members of the BATT program and the battery community to characterize these and related systems (e.g., W.S. Yoon; XAS of $\text{LiCo}_x(\text{Ni}_{0.5}\text{Mn}_{0.5})_{1-x}\text{O}_2$; M.S. Whittingham, magnetic susceptibility studies of $\text{Li}_x(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$; TEM + electrochemistry, Y. Shao-Horn; J. Goodenough, $\text{Li}(\text{Ni}_{0.5+\delta}\text{Mn}_{0.5-\delta})\text{O}_2$). Work is also ongoing on the thermal stability of layered oxides and the factors that control structure and electron/ Li^+ -ion mobility in LiFePO_4 .

¹ "Electrodes with High Power and High Capacity for Rechargeable Li Batteries," K. Kang, Y.S. Meng, J. Breger, C.P. Grey and G. Ceder, *Science*, **311**, 977-980 (2006).

Battery Materials: Structure and Characterization

Won-Sub Yoon and Xiao-Qing Yang
Brookhaven National Laboratory

The primary objective is to develop and apply advanced diagnostic techniques to determine the contributions of electrode material changes, interfacial phenomena, and electrolyte decomposition to cell capacity, power decline, and abuse tolerance. The results of these studies will be used to guide the exploratory research for new cathode, anode, and electrolyte materials for high power lithium batteries.

The key elements of this BATT program at BNL are the extensive collaborations and the continued development of new diagnostic tools for battery material studies. In the past year, we have carried out *in situ* XRD studies on doped spinel for Prof. Manthiram's project (as suggested at the FY2005 BATT review) and on layered-spinel $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMn}_2\text{O}_4$ electrodes for Dr. Thackeray's project. *In situ* XAS studies were also carried out on this material and the preliminary results indicate that during initial charge to high voltages (5V), Li and/or Li_2O are extracted from the structure at distinct voltages and Mn^{4+} ions are reduced during discharge in activating the Li_2MnO_3 component. We also have collaborations with other members of the BATT team such as Prof. Grey, Prof. Ceder, and Prof. Whittingham. Collaborations with industry partners such as MER Corp. (on low temperature electrolytes) and LG Chemical Corp. (on cathode material studies) have also been established. On the new diagnostic tool development, we have built a new sample stage that can allow for the control of temperature from -20°C to 100°C for *in situ* XRD and XAS experiments.

The *in situ* and *ex situ* X-ray absorption experiments at O, P, and Fe K-edge were performed on $\text{Li}_{1-x}\text{Fe}_{1-y}\text{Mn}_y\text{PO}_4$ electrodes (from Dr. Zaghbi in Hydro-Quebec) and other LiFePO_4 -based materials with different x values. It was found that the major charge compensation during Li deintercalation is achieved by the oxidation of Fe^{2+} ions at lower potential (~ 3.6 V) and the oxidation of Mn^{2+} ions at higher potential (~ 4.1 V). The interesting new observation is that the chemical changes beyond the first coordination sphere around the phosphorus atoms have a systematic influence on the P K-edge XANES spectrum. No pre-edge peak was observed in P K-edge XANES spectrum for the pristine LiFePO_4 . However, upon Li deintercalation, pre-edge peaks start to appear in the lower energy region of the main edge. The gradual increase of pre-edge peak intensities with the Li-ion extraction shows that these pre-edge peaks are due to the hybridization of P 3p states with the Fe 3d states. Preliminary results of the *in situ* XRD studies for LiFePO_4 at low-temperature provide us with a useful tool to monitor the structural changes and the rate capability of this material operating at low temperature. The layered $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ system has been studied using Synchrotron-based XRD and XAS techniques to investigate the electronic and structural changes during the electrochemical cycling process. It was found that the structural stability of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ is higher than $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, which in turn is higher than LiNiO_2 , as reflected in the suppression of hexagonal 3 (H3) phase. The major charge compensation mechanisms in the $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrode system on Li-ion deintercalation are established using the combination of hard and soft XAS analysis. The major charge compensation at the metal site during charge is achieved by the oxidation of Ni^{2+} ions, while the manganese ions remain mostly unchanged in the Mn^{4+} state. A large portion of the charge compensation during Li-ion deintercalation is attributed to the oxygen sites which are associated with the presence of Co. The results of these studies have been published or accepted for publication by prestigious journals such as JACS, Electrochemical and Solid-State Letters, and Electrochemistry Communications.

In the future, more studies on new alloyed anode systems and functional electrolytes will be studied in collaboration with our industry partners using our synchrotron-based techniques.

Materials Characterization and Cell Building

Vincent Battaglia

Lawrence Berkeley National Laboratory

The mission of this task is to support the other BATT program PIs by characterizing and assessing materials developed against defined baselines. The task consists of two interrelated efforts: 1) the physical, chemical, thermal, and electrochemical assessment of materials, and 2) the establishment of a representative and robust cell design. Below is an update of the progress made in these two areas over the past year.

Materials Characterization – The key properties that relate battery materials to battery performance can be organized into four categories: 1) physical characterization, 2) chemical characterization, 3) thermal characterization, and 4) electrochemical characterization. The laboratory is being set-up to perform all of the above, and hence, provide a comprehensive, independent, and reliable analysis of advanced cell materials developed within the program.

Physical characterization. Physical characterization consists of measuring the surface area through BET, the particle size distribution through PSA, and assessing the microscopic structure through SEM. Over the past year the characterization of 18 materials, which includes 7 cathodes, 6 anodes, and 5 conductive additives has been completed. Each measure is made at least three times to ensure reproducibility.

Chemical characterization. As of today, chemical characterization consists of measuring the dissolution of a candidate cathode material in a typical Li-ion electrolyte. To date, a set of experiments has been defined and initiated. This effort was delayed while trying to identify a laboratory with ICP-MS capability willing to test samples with possible fluorine contamination.

Thermal characterization. Li-ion batteries have exhibited warning signs when it comes to abuse tolerance. It has been shown that the thermal response of materials subject to temperatures around 100°C can result in a thermal run-away event. It has also been demonstrated that the cathode and anodes can go into such an event at a lower temperature in the presence of electrolyte. During the past year, an old accelerated rate calorimeter (ARC) sent to the lab from SRI by DOE has been upgraded to a useable state. As of this writing, the ARC has been calibrated.

Electrochemical characterization. Electrochemical testing of materials is of little value if the medium in which they are to be tested is contaminated. To address questions of water and carbon dioxide contamination during fabrication or testing, the sealing and fabrication techniques have been upgraded. A new sealer and new pouch material have been obtained and tested. An order of magnitude improvement in electrolyte loss when stored at 45°C has been measured. The battery fabrication lab has been redesigned such that all of the equipment has been placed in boxes of inert atmospheres.

Cell Building: Electrochemical testing is also of little value unless it is performed in a robust and representative cell configuration. A comprehensive approach to cell making is underway. The intent is to include the macroscopic cell modeling capabilities of Dr. Srinivasan with the structural models of Dr. Sastry in the design of cells. The parameters of Dr. Sastry's model are established by measuring the conductive properties of each component and of composites of subsets of the components. Using a four point probe, the conductivity of films of polymer, polymer with amorphous carbon, and polymer with amorphous carbon and graphite have been measured for different weight fractions of polymer. Methods of combining materials are also being investigated. The conductivity and performance of complete electrodes will be tested and the results compared to the models of Dr. Sastry and Dr. Srinivasan in the next few months.

Lithium-Ion Polymer Batteries with Low-Cost Materials

Karim Zaghib

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A major effort was undertaken to resolve problems in the cell assembly procedure. Some of the steps were modified and additional steps were introduced in the protocol. We are now able to completely control all of the assembly steps to fabricate laminated Li-ion cells.

The second goal was focused on developing a water soluble binder (WSB) and cathodes containing LiFePO_4 . Studies were completed on optimization of the HQ process for using water soluble binder in negative electrodes containing natural graphite (NG), hard carbon (HD) soft carbon (SC) or $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO), as well as positive electrodes with LiFePO_4 . Cathode electrodes with a new generation of LiFePO_4 material and WSB were evaluated in laminated lithium and lithium-ion cells.

A new generation of LiFePO_4 powder cathode material was received from Phostech. This powder has a small particle size: the primary particles are less than 200 nm. This LiFePO_4 was recently introduced in our electrode studies. After resolving problems with the cell assembly procedure, the performance of our laminated cell was studied. Good cycling performance was obtained with this cathode material discharged at C/1 and charged at C/6, even at 60°C. Less than 1% capacity fade after 200 cycles was observed. Furthermore, the WSB binder appeared to be stable at this temperature.

We studied the effect of gel polymer formation on cell performance. The high-power capability of the Li-ion laminated cell in the gel configuration showed comparable results to a liquid cell up to a 4C discharge rate. At high rate, > 4C, a noticeable difference in the Ragone plot is observed between liquid and gel cells. The rated capacity in the gel cells was 20% lower than the liquid cells at 10C.

Accomplishments

- Problems in the cell assembly procedure of laminated cells were resolved.
- A new generation of LiFePO_4 with small primary particle size for cathode material was introduced.
- Studies on the optimization of the HQ process using water soluble binder for negative electrodes (NG, HC, SC LTO) and the positive electrode (LiFePO_4) were completed.
- Characterization of a new generation of LiFePO_4 at 60°C is underway. Good cycling stability and high-power performance were obtained. Post mortem analysis of the cycle D electrode was completed
- Characterization of the laminated Li-ion and Li metal cells with liquid and gel polymer electrolyte is in progress. Promising discharge rates were obtained with the laminated Li cells.
- 20 Li-ion gel-type cells and coin-type cells were prepared and delivered to LBNL for evaluation.
- Preliminary data on ionic liquid with TSI and FSI were obtained, and the results will be presented in the poster section.
- HQ technical staff made two visits to LBNL to establish better collaboration and to improve technology exchange (Nov 2005 and April 2006). Laminated cells containing liquid and gel electrolytes were prepared by HQ staff during their visit to LBNL, and cycling studies of these cells were initiated.

Design, Optimization, and Fabrication of Li-ion Electrodes for High-Power Applications

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Our objective is to determine morphologies and material combinations that improve high-rate HEV performance for BATT-program cathodes, and to better understand the physical processes that decrease electrode performance. Essentially, this means identifying where voltage losses occur and finding ways to eliminate them. Our main effort this year has been investigating the effects of using carbon fibers as a conductivity additive in LiFePO_4 cathodes. Other long-term efforts include examining the effect of different current-collector morphologies, experiments and modeling to better understand inter-particle connections, and developing new diagnostic tools for electrolytes.

Carbon-fiber additive. For our carbon-fiber work we compared baseline LiFePO_4 cathodes containing carbon black and graphite additives with cathodes in which some or all of these carbon materials were replaced with fibers. We used vapor-grown carbon fibers, obtained from Pyrograf Products, with diameters in the range 70-200 nm and lengths in the range 50-100 μm . The fibers are heat treated to increase carbon ordering, and thus conductivity. We have shown that substitution of fibers leads to greater power performance. However, even in the case of the baseline cells it appears that USABC goals for HEV power can be met with a modest amount (8% by weight) of conductive carbon additive in LiFePO_4 cathodes. We showed that the optimum active-material loading for power performance is around 1 mAh/cm^2 for the carbon levels used. The conclusion is that “thin” cathodes do not generate the highest specific power, once the weight of non-active materials (like the current collector and packaging) are taken into account.

HEV cycle-life testing. We have begun HEV cycle-life testing of the cells with different carbon compositions. As determined by the area specific impedance (ASI), the fiber-containing cells have better performance over the tested range of around 20,000 short-pulse cycles. However, all the compositions showed a similar (and unacceptable) impedance rise with time, suggesting that the same degradation mechanism was at work in each. We are beginning a series of experiments to elucidate that mechanism. One type of experiment is to determine what portion of the impedance rise is due to degraded electronic conduction in the carbon network and at the current collector. Preliminary work indicates that resistance at the current collector is not an insignificant component of the overall impedance.

Other related efforts. We have developed a modeling approach for inter-particle contact that can be integrated into the battery-modeling codes of BATT researchers to better predict cell performance. In an associated experimental effort, we are using atomic force microscopy to explore the nature of the point-to-point connections between active-material particles and carbon particles and fibers. Finally, we continue to work through instrumentation challenges that arise in the development of a new Hall-effect-based tool to directly measure ion transference numbers—an electrolyte mass-transport property that is difficult to obtain.

Scale-Bridging Simulations of Active Materials in Li-ion Batteries, and Validation in BATT Electrodes

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Promising battery chemistries are limited by practical, manufacturing limits, which include the processing and post-processing of active materials. Dramatic improvements have been achieved in the high-rate performance and capacities of Li-based cells, including the BATT baseline chemistries (LiFePO_4 , LiMn_2O_4 , $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, and $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Al}_{0.05}\text{O}_2$). However, different realizations of cells have produced different performances, which depend substantially upon the density, shapes, and type of conductive additives in the cathode. The ranges in types (carbon black and graphite), shapes (spherical and platelet), and processing steps (coated or noncoated, calendared, etc.) of additives and electrodes, offers both a challenge and opportunity to designers, in developing rational, multiphysics models of their performance in the cell.

In our work, we have three central objectives:

- 1) Determine superior composition and processing conditions of electrodes for conductivity enhancement, especially for the LiFePO_4 cathode.
- 2) Develop scale-bridging simulations that allow identification of the best particle morphologies for both energy- and power-dense systems.
- 3) Develop superior anodes and cathodes by altering the content and morphologies of conductive materials.

To meet the first objective, we have used our previously developed techniques in experimental characterization of conductivity, to determine the properties of materials used within the BATT program. These include LiFePO_4 , LiMn_2O_4 , $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, and $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Al}_{0.05}\text{O}_2$, whose conductivities range widely. In determining processing scenarios which provide improved conductivity, mechanical stability, and surface area, we have also developed new modeling techniques for packing, conduction, mechanics, and electrochemical performance of porous systems.

These techniques also have been used to meet our second objective, in development of scale-bridging simulations allowing selection of particle types and properties. We have examined the constituents of the baseline systems, and built models to simulate cathodes, over a realistic range of porosities. We found a strong correlation between the volume of packed conductive additives and conductivity; and our simulations suggest that specific fractions of conductive additives (e.g., carbon black and graphite) maximize conductivity, given the shapes and sizes of active material particles. A dynamic collision model, developed previously, was used to generate realistic morphologies of composite electrodes. Then, a commercial finite element analysis package was used to analyze the stress distributions, along with a new model developed this year, to analytically determine stresses due to intercalation. Our results allow direct comparison, and superposition, of mechanical forces due to electrode compression and intercalation.

A 3D finite element model has also been completed to simulate the electrochemical performance of a model $\text{Li/PEO:LiClO}_4/\text{LiMn}_2\text{O}_4$ system. This new simulation is capable of incorporating realistic particle morphology in modeling of cell performance, and our findings confirm the importance of packing architecture on charge distribution. We have now established that particle morphology plays a significant role in electrochemical conductivity, due to the size of particles used for conduction relative to electrode thickness. Our next steps, in meeting our third objective, include investigation of the relationship between electrode particle shapes on high power and energy capabilities and lifetimes of composite cathodes, and selection of materials for other BATT workers.

Corrosion of Aluminum Current Collectors

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Our efforts during the past year were primarily focused on inspecting aluminum current collectors in life-tested ATD batteries for evidence of corrosion. In addition, we have investigated details of the mechanism of corrosion of Al current collectors in Li-ion batteries.

We have meticulously examined aluminum current collectors of 19 ATD batteries from GEN2 series that were previously charge/discharge tested at different temperatures ranging from (approximately) 25-60°C. Microscopic inspection of aluminum current collectors of the ATD batteries was undertaken to detect evidence of corrosion. Earlier laboratory corrosion tests of aluminum and the results of microscopic inspection of life-tested Li-ion coin cells indicated aluminum current collectors were susceptible to crevice corrosion. That is, aluminum bonded to battery cathodes, which are deliberately made microporous to enhance lithium insertion and removal, was susceptible to underdeposit corrosion (a form of crevice corrosion) when exposed to electrolyte at pores in the cathode.

The optical and scanning electron microscopy indicate unambiguously that the aluminum current collectors of the ATD cells are pitted. Some pits, referred to as mechanical pits, were formed during the attachment of the cathode. Corrosion pits formed during cycling of the batteries. The number and size of the corrosion pits increase with cycling time. The area fraction covered by mechanical pits is approximately 5-6%. The area fraction covered by corrosion pits was approximately 12% following cycling at 25°C for 140 weeks. There was a very strong correlation between the fraction of area corroded and the power fade and capacity fade of the ATD Cells, as well as between the pits density and the power fade and capacity fade. This correlation suggests the contribution of corrosion to power fade and capacity fade.

There are at least three adverse consequences of the corrosion of the current collectors. First, corrosion will decrease the effective surface area of the current collector. Second, the solid corrosion products, which fill the pits, are themselves heavily cracked and might cause cracking of the cathode, which is expected to cause a significant increase in power fade. The cracking of the cathode might also occur because of the stresses resulting from the greater volume of the solid corrosion product compared to the volume of the aluminum that was corroded. Third, the high concentration of aluminum (2,500 - 3,000 ppm) that was measured in the electrolyte of the ATD cells is presumably a consequence of corrosion of the current collectors and might be expected to significantly impair the performances of the anode and cathode.

Our future plans are to study the mechanism of corrosion of the current collectors, and to identify and evaluate remedial actions that will reduce/eliminate corrosion of the current collectors. In particular we will focus on determining (1) the compositional changes in the local electrolyte that are responsible for the localized corrosion of the aluminum; (2) the mechanism of propagation of the corrosion pits; (3) how the solid corrosion products cause cracking of cathode; and (4) the effects of soluble aluminum corrosion products on the performance of the battery. In investigating remedial actions, we would pursue two paths: (1) determining if prepassivation of the aluminum current collector (e.g., in LiPF_6 and LiBOB) can prevent corrosion without impairing battery power fade, and (2) if mixed salt electrolytes can prevent corrosion of the current collector without reducing battery performance.

We also plan to perform analyses of corrosion of the current collectors as part of the diagnostic work related to GEN3 ATD cells.

Microstructure and Transport Properties of Cathode Materials

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Application of nanoparticle coating on the positive electrode materials shows promise to stabilize Mn-based positive electrodes during electrochemical cycling. We are currently preparing and characterizing 'AlPO₄' coated LiMn₂O₄ and LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ samples. Combined TEM, STEM and SEM imaging and X-ray mapping have shown that the thickness of the 'AlPO₄' coating varies from 5-10nm to 50-100nm, which is clearly revealed in the TEM image below. Our study has shown, for the first time, that the coating is not single-phase AlPO₄, rather consisting of P-rich thick regions (50-100nm) and Al-rich thin regions (5-10nm). Understanding the coating microstructure is key to understand and explain its effect on electrode properties. EIS measurements of two-electrode Li/LiCoO₂ cells have shown that 1) the electronic resistance decreases sharply for the coated oxide electrode (the bottom right graph) upon first charge in comparison to the bare oxide electrode (the top right graph); 2) the electronic resistance of the coated oxide electrodes appears to be lower than that the bare oxide electrode but further experiments needed to verify the result (as shown below, the low-frequency peak considerably changes as a function of voltages). This difference is significant for the rate performance of these materials. We have developed a three-electrode Li/LiMO_x cell configuration for EIS measurements and we are currently collecting EIS data to verify the findings based on two-electrode cell setup, which will be employed to study and compare transport properties of coated LiMn₂O₄ and LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ with coated LiCoO₂.

